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(54) New catalyst components for the polymerization of alpha-olefins and catalysts obtained therefrom.

(57) Catalyst components for the polymerization of alpha-olefins and of the mixtures thereof with minor amounts of ethylene that are obtained from emulsions or dispersions in an inert liquid medium or in an inert gaseous phase of a liquid phase comprising compounds or compositions containing Ti and Mg compounds, which are immiscible in aliphatic hydrocarbons or comprise a catalytic component precursor which is also immiscible in aliphatic hydrocarbons.

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Object of this invention are new catalyst components  
5 for the polymerization of alpha-olefins and of mixtures  
thereof with minor amounts of ethylene and the catalysts  
obtained therefrom.

More particularly, the invention refers to new catalytic  
10 components obtained from emulsions or dispersions in  
an inert liquid medium or in an inert gaseous phase of a  
liquid phase comprising compounds or compositions containing  
15 Ti and Mg compounds, which are immiscible in aliphatic  
hydrocarbons, and the use of the catalysts obtained  
therefrom in the polymerization of alpha-olefins  $\text{CH}_2=\text{CHR}$   
in which R is an alkyl radical having from 1 to 6 carbon  
atoms, particularly propylene, or of mixtures thereof with  
minor amounts of ethylene.

It is known that the coordination catalysts commonly  
20 used in the industrial practice are heterogeneous systems  
obtained by reaction of a transition metal compound (generally  
25 a Ti halide) with an organometal compound of the metals of Groups I-III of the Periodic System.

The transition metal compound used for the preparation  
of the catalyst is generally a solid insoluble in the  
hydrocarbon polymerization medium or is a liquid soluble  
30 in said medium.

Homogeneous coordination catalysts (soluble in the  
polymerization medium at least before the polymerization  
35 is started) are also known.

These systems, however, have not been adopted in the  
industrial practice because of the fact that the activity

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thereof, that at the beginning is also very high, decreased  
5 rapidly and this does not allow to obtain high polymer  
yields.

Within the field of heterogeneous catalysts, supported  
catalysts have been adopted in the industrial practice al-  
ready since some time, which are endowed of so high activi-  
10 ty as to allow to avoid the expensive depuration treatments  
of the polymer from the catalytic residues.

These catalysts are generally obtained from a catalytic com-  
ponent comprising a titanium compound supported on a magne-  
15 sium halide in active form.

Catalysts supported on Mg halides endowed of both  
high activity and stereospecificity that are suitable for  
the stereoregular polymerization of propylene and similar  
20 alpha-olefins are also known. These catalysts comprise in  
general a titanium compound supported on a Mg halide in ac-  
tive form, modified with electron-donor compounds.

In the modern industrial processes using "high yield"  
25 supported catalysts the requirement is felt of being in po-  
sition to have available catalysts having a controlled mor-  
phology and particle size, which be capable to yield a po-  
lymer in form of particles which maintain the morphology  
and the particle size of the catalyst and that, furthermore,  
30 be endowed with a high flowability and bulk density.

A catalyst having these characteristics shows advanta-  
ges not only during polymerization and makes easier the sub-  
sequent operations of transfer and/or treatment of the poly-  
35 mer but can also allow to eliminate the granulation step of

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5 the polymer, this operation being one that, as it is known,  
requires large amounts of energy.

The methods employed until now for the preparation of  
catalysts having a controlled morphology and/or particle size  
are based on operations expensive per se, which comprise  
10 the preformation of a precursor of the catalytic component  
in form of particles having a controlled morphology and the  
subsequent transformation of these particles to obtain the  
true catalytic component or the precipitation of the catalytic  
15 component in conditions in general very critical, followed  
by the operations of separation, washing and drying of  
the solid.

According to other methods, precursors of the catalytic  
20 component in the melted state are emulsified in an inert  
immiscible liquid and the emulsion is then subjected to  
quenching to obtain the solidification of the dispersed liquid  
phase which is subsequently treated for the transformation  
of the solid.

25 Examples of these methods are described in the applicant's U.S. patent 3,953,414 and Belgian patent 878,347.

Coordination catalysts are not known hitherto wherein  
the component comprising the transition metal compound, con-  
30 sisting of a liquid immiscible in the conventional solvents  
used in the polymerization processes, be employed in emul-  
sion and dispersion form in said liquid medium.

It has been now unexpectedly found that it is possi-  
35 ble to obtain catalysts suitable to produce crystalline

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polymers of the alpha-olefins and crystalline copolymers  
5 thereof with minor amounts of ethylene, in the form of par-  
ticles having controlled morphology and/or particle size,  
by carrying out the preparation of the catalytic component  
10 comprising the transition metal compound by starting from  
emulsions or dispersions in an inert liquid medium or in an  
inert gas phase of a liquid phase comprising compounds or  
compositions containing Ti and Mg compounds that are immi-  
scible in the normal aliphatic hydrocarbons or comprising  
15 a precursor of the catalytic component which is also immi-  
scible in the aliphatic hydrocarbons.

The transformation of the above indicated emulsions  
or dispersions in the catalytic component having controlled  
morphology and/or particle size takes place by reactions  
20 which involve the formation of a solid phase comprising a  
titanium compound supported on a magnesium halide.

Preferably and in order to endow the catalyst of a  
higher stereospecificity, it is worked in conditions whe-  
25 rein the solid phase obtained by transformation of the di-  
spersed liquid phase comprises also an electron-donor com-  
pound.

Electron-donor compounds suitable for this purpose  
30 are well known in the literature.

As example can be cited the compounds described in  
the applicant's U.S. patents 4,107,414 and 4,107,418. Other  
examples are described in the applicant's European patent  
applications 81/106301, 81/106300 and 81/106299.  
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5 Any reaction that leads to formation of a solid phase comprising a titanium compound supported on a magnesium halide is suitable for the transformation of the above described emulsions or dispersions.

10 Examples of known reactions are those wherein the Ti and Mg components forming the dispersed liquid phase are made to react with an Al-alkyl compound having formula  $ALR_{m,n}^X$  wherein R is an alkyl, cycloalkyl or aryl radical containing from 1 to 18 carbon atoms; X is a halogen; m is a number comprised between 1 and 3; n is a number comprised between 15 zero and 2.

20 According to other methods, the Ti and Mg compounds comprising also an Al halide are made to react with compounds such as for example diisoamyl ether, alkyl-arylether such as for example anisol that are capable of forming complexes with the Al halide but not with the Mg halide.

25 Al already indicated, any compound or composition comprising Ti and Mg compounds that is immiscible in aliphatic hydrocarbons is suitable for the formation of emulsions or dispersions employable for the preparation of the catalytic components of the invention.

30 Similarly, any precursor of the catalytic components that in the liquid state is immiscible in aliphatic hydrocarbons is suitable for the preparation of the emulsions or dispersions from which to obtain the catalytic component.

35 Examples of compounds or compositions and methods of preparation thereof, that are suitable for obtaining the

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5 emulsions and suspensions are as follows.

Anhydrous magnesium halide, in particular  $MgCl_2$ , is made to react with an anhydrous aluminum halide, in particular  $AlCl_3$ , in an aromatic hydrocarbon, in particular toluene, in the presence of a halogenated hydrocarbon, preferably 10 1,2-dichloroethane. To the oily liquid thus obtained (now immiscible in the same aromatic hydrocarbon) a titanium compound, in particular  $TiCl_4$ , is added. An oily liquid is obtained that is immiscible in the common aliphatic hydrocarbons.

More particularly, the Mg and Al halides and the aromatic hydrocarbons are made to react at the reflux temperature of the aromatic hydrocarbon in the Mg/Al/toluene molar ratio of 1:3:12.

To this suspension the halogenated hydrocarbon is added in the ratio of about 2 mols per mol of Mg halide and it is heated until an oily liquid is formed. Then the Ti compound is added in a Ti halide/Mg halide molar ratio comprised in general between 0.1:1 and 1:1.

The oily liquid that is obtained before the addition of the Ti compound is in itself a precursor of the catalytic component that can be emulsified and the emulsion be treated for the transformation to catalytic component.

In the above indicated preparation the Al trihalide can be substituted by an alkyl Al dihalide, the toluene by benzene, xylene and by similar aromatic hydrocarbons;

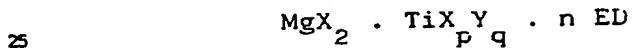
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5    1,2-dichloroethane can be substituted by  $C_2H_5Cl$ ,  $C_3H_7Cl$ ,  
 $n-C_4H_9Cl$ ,  $s-C_4H_9Cl$ ,  $t-C_4H_9Cl$ ,  $C_6H_5Cl$ ,  $CHCl_3$ ,  $C_6H_5CH_2Cl$ ,  
 $CH_3Cl_2$  and by similar alkyl or aryl halides.

10    Another method of preparation consists of dissolving  
an anhydrous Mg halide in a  $Ti$  tetraalcoholate, in particu-  
lar  $Ti$  tetrabutylate and of making an anhydrous gaseous  
hydrohalogenic acid to flow in the solution until separa-  
tion of an oily phase.

15    According to a modification of the above described  
method, the hydrohalogenic acid can be replaced by an acyl  
halide, in particular acetyl chloride. The butyl acetate  
that is formed is partly removed until formation of an oily  
liquid.

20    Other compounds suitable for the preparation of the  
emulsions or suspensions from which the catalytic components  
of the invention are obtained, can be selected from the com-  
pounds having the formula:



30    that in the liquid state be immiscible in aliphatic hydro-  
carbons. In the formula X is a halogen atom; Y is a OR ra-  
dical in which R is an alkyl, cycloalkyl or aryl group con-  
taining from 1 to 18 carbon atoms; p is a number from 1 to  
4; q is a number from zero to 3;  $p+q = 4$ ; n is a number  
from 3 to 6; ED is an electron-donor compound selected in  
particular from the esters of carboxylic aliphatic or aro-  
matic acids.

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5 Examples of these compounds are:  $MgCl_2 \cdot TiCl_4 \cdot 4Ac$   
 $(Ac=CH_3COOC_{2,5})$ ,  $MgCl_2 \cdot TiCl_4 \cdot 4EB$  (EB = ethylbenzoate),  
 $MgCl_2 \cdot TiCl_2(OC_{2,5})_2 \cdot 4C_{2,5}OH$ ,  $MgCl_2 \cdot TiCl_4 \cdot 5POCl_3$ .

10 These compounds are prepared according to known methods, by dissolving the Mg halide in the ED compound, by adding to the solution the stoichiometric amount of the Ti compounds and by then causing the reaction to take place at reflux. The excess of ED compound is at the end removed by evaporation.

15 The precursors of the catalytic components are selected in general from the adducts of the Mg halides comprising an electron-donor compound, in particular an aliphatic, cycloaliphatic or alkylaryl alcohol. Adducts of this type and the methods of preparation thereof are known in the literature. These adducts are in general solids at room temperature but have a relatively low melting point.

20 They are emulsified, in the liquid state, in an inert liquid; the emulsion is then made to react, according to known methods, with reagents capable of transforming the adduct in active catalytic component.

25 Examples of transformation reactions to catalytic component are those wherein the adduct is made to react directly with  $TiCl_4$  or, before the reaction with  $TiCl_4$ , is made to react with an Al-alkyl compound or with halogenated silicon compounds such as  $SiCl_4$  and halosilanes. These and other reactions are described in the Belgian patents

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5 857,574 and 878,347.

In order to improve the stereospecificity of the catalyst, the reactions are carried out in the presence of an electron-donor compound capable of forming adducts with the Mg halide.

10 The emulsifying of the liquid Ti compounds as well as of the precursors can be carried out according to known techniques. Preferably the transition metal compound is dispersed into an oil of parafinic, naphthenic, aromatic or silico-  
15 nic type and then subjected to the transformation reactions.

Examples of these oils are silicon oil Baysilon M 100 (Bayer), vaselin OE 55 (ROL), Cortis OB 55 oil (Total), Circosol 2XH oil (Sunoco) and Dutrex R 55 oil (Shell).

20 In some cases, in particular when the emulsion were unstable in the time, it has been found convenient to prepolymerize small amounts of ethylene or other olefin. The prepolymerization is carried out in general until a few grams of polymer (1-100 g) per gram of catalytic component  
25 are formed.

The obtained prepolymer is then treated with an ether solution in an aromatic hydrocarbon in order to obtain the active catalytic component.

30 In some cases it proved convenient to cause the adsorption of the immiscible liquid phase used for the preparation of the emulsions or dispersions, to take place on a porous inert support having predetermined geometric  
35 form and/or particle size distribution. The solid is then

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5 suspended in an inert liquid medium, that is immiscible with the adsorbed liquid phase and the suspension is then treated for the transformation to the catalytic component.

10 The co-catalysts usable with the catalytic components of the invention to obtain the catalysts for the polymerization, according to known methods, of alpha-olefins and of mixtures thereof with minor amounts of ethylene comprise Al-alkyl compounds such as Al-trialkyl, hydrides of Al-alkyl and, preferably, electron-donor compounds which, as it is known, improve the stereospecific characteristics of the catalytic system. Examples of Al-alkyl compounds are Al-triethyl, Al-triisobutyl, Al-tri-n-butyl.

20 Examples 1-4

1) Preparation of emulsifiable liquid A.

25 The emulsifiable liquid employed in all examples 1-4 was prepared in the following conditions and modalities. 44.07 g of anhydrous  $MgCl_2$ , 199 g of anhydrous  $AlCl_3$ , 640 cc of anhydrous toluene and 80 cc of dehydrated 1,2-dichloroethane were introduced into a flask fitted with stirrer, dropping funnel, reflux condenser and thermometer, after previously flushing with nitrogen. The 30 suspension was heated to 110 °C and maintained at this temperature for 2 hours. The suspension was then cooled to room temperature and filtered: 765 cc of a red-brownish oily liquid were obtained.

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5        2) Emulsifying of liquid A.

The device for the emulsifying of liquid A comprised a Keller type flask fitted with dropping funnel and thermometer, in which a turbostirrer turning at a speed of 12,000 r.p.m. was inserted.

10      The control of the temperature was carried out by immersion of the flask in a methanol/dry ice cooling system. Silicon oil (Baysilon M 100 of Bayer) and n-butyl ether were introduced into the flask, after a previous 15 flushing thereof with nitrogen. Then liquid A (to which  $TiCl_4$  was previously added) was fed under the highest stirring while cooling simultaneously, within 5 minutes and while maintaining the temperature at the desired value. The stirring was continued for another 10 minutes.

20      The data of the preparation are reported in Table 1.

25        3) Reaction with  $Al(C_2H_5)_3$  and prepolymerization.

The whole volume of the emulsion prepared in 2) was transferred within the time of about 3 minutes to a flask fitted with dropping funnel and thermoregulated, wherein a 500 cc hexane solution containing each time the amount of  $Al(C_2H_5)_3$  (TEA) equal to the Al/Ti ratio reported in Table 1 was previously introduced. The reaction temperature is also reported in Table. In the resulting suspension ethylene was flowed for a few minutes in order to remove 30 nitrogen and then the flask was pressurized with ethyle-

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ne at an over-pressure of 20-60 mmHg, for a time of 30 minutes. A prepolymer was recovered that was then washed with hexane and dried under vacuum at 50 °C for 3 hours.

10 4) Polymerization of propylene.

The polymerization tests were carried out in a 2.5 liter autoclave fitted with stirrer and thermocouple. 1000 cc 15 of an hexane suspension containing the amounts of Al-triethyl and phenyltriethoxysilane (FES) indicated in Table 2 were introduced under nitrogen atmosphere into the autoclave previously heated at 60 °C.

20 The autoclave was then closed, hydrogen was introduced up to a pressure of 0.2 atm., the temperature was increased to 70 °C and propylene was introduced up to a 25 pressure of 7 atm. The pressure was maintained constant during the polymerization by feeding the monomer continuously. After 4 hours the test was interrupted; the solid polymer was separated from the solvent by filtration 30 and then dried under a nitrogen flow at 70 °C. In all tests the polymer was present in form of particles having a controlled morphology and particle size. The performance of the catalyst and other characteristics of the polymer are reported in Table 2.

35 The isotacticity index reported in Table 2 is related to a polymer insoluble in the polymerization medium.

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Table 1

Example	Emulsifying			Reaction with AlEt <sub>3</sub>			Percent composition prepolymer (% by weight)		
	Sil. oil (cc)	n-butyl ether (cc)	Emulsifiable liquid	Al/Ti	Temperature °C	Prepolymer weight (g)	Ti	Mg	C1
	Liquid A (cc)	TiCl <sub>4</sub> (cc) <sup>4</sup>							
1	50	2.9	50	1.85	6	60	5.9	8.7	40.15
2	80	6	80	3.0	4.5	50	28.8	2.95	5.9
3	100	7.5	100	1.0	8	50	13.1	2.45	9.1
4	100	7.5	100	1	11	40	10.2	3.5	29.8

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10  
5Table 2

Example	Catalytic component (g)	$\text{AlEt}_3$ (mMols)	FES (mMols)	Yield (g. polymer/g Ti)	Isotactic index (%)	$\langle \eta_r \rangle$ (dl/g)
1	0.148	5	0.25	6,000	91.5	1.3
2	0.240	5	0.25	5,200	93	1.1
3	0.203	5	0.25	12,700	93	1.28
4	0.238	5	0.25	2,500	91.6	1.3

Example 5

5      4 g of prepolymerized catalytic component obtained according to example 3 were added to 25 cc of toluene containing dissolved 0.0088 M of anisol. The suspension was heated at 60 °C for 3 hours.

10     Then it was cooled to room temperature and filtered; the solid was washed with n-heptane and dried under vacuum at 50 °C for 3 hours.

15     0.2 g of the solid were used in a polymerization test carried out in the conditions of examples 1-4. 157 g of polymer were obtained, of which the fraction insoluble in the polymerization medium is in form of particles having controlled particle size, with the size comprised mainly between 500 and 1000 micron.

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C L A I M  
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1) Solid components of catalysts for the polymerization of alpha-olefins  $\text{CH}_2=\text{CHR}$  wherein R is an alkyl radical containing from 1 to 6 carbon atoms and of mixtures thereof with minor amounts of ethylene, obtained by transformation reactions of the dispersed liquid phase to solid phase comprising a Mg halide and a Ti compound, starting from emulsions or dispersions in an inert liquid medium or in an inert gas phase of a liquid phase comprising compounds or compositions containing Ti and Mg compounds that are immiscible in aliphatic hydrocarbons or comprising a precursor of the catalytic components that are also immiscible in the aliphatic hydrocarbons.

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European Patent  
Office

EUROPEAN SEARCH REPORT

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Application-number

EP 82 11 1903

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.?)
D, A	US-A-3 953 414 (P. GALLI et al.) * Claims 1-13 *	1	C 08 F 10/00 C 08 F 4/64
A	EP-A-0 018 737 (MITSUI) * Claims 1-12 *	1	
A	FR-A-2 428 056 (MITSUBISHI) * Claims 1-6; example 1 *	1	
A	US-A-4 218 339 (U. ZUCCHINI and I. CUFFIANI) * Claims 1-21; column 2, lines 52-68 *	1	
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			TECHNICAL FIELDS SEARCHED (Int. Cl.?)
			C 08 F
<p>The present search report has been drawn up for all claims</p>			
Place of search <b>THE HAGUE</b>	Date of completion of the search <b>30-03-1983</b>	Examiner <b>WEBER H.</b>	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			